

REMARKS

Claims 1, 2, 5-23, 25-34, 36 and 38-40 are pending in the above-identified application. Claims 2, 9-11, 18, 19, 30 and 31 have been indicated to be in allowable form, and are merely objected to as depending upon a rejected base claim. Note that a Preliminary Amendment was filed on January 27, 2003 and it is requested that this Preliminary Amendment be taken into account in the next communication issued by the Patent Examiner.

Various claims have been amended in accordance with the helpful suggestions stated in the Office Action, as well as in response to the issues raised under 35 U.S.C. 112.

Removal of Claims Objections

Claims 1, 7 and 15-24 have been objected to as indicated at page 2 of the Office Action. These claims have been amended in accordance with the helpful suggestions stated in the Office Action such that these objections should now be withdrawn.

Issues Under 35 U.S.C. § 112 and 101

Claim 3 has been rejected under 35 U.S.C § 112 as allegedly failing to be enabled by the disclosure of the present specification because of the terpene skeleton-containing epoxy resin of formula (II) recited therein. Specifically, the Office

Action states that the compound of formula (II) does not contain a terpene structure.

The above-rejection is respectfully traversed. Specifically, note that the center, non-aliphatic ring structure with the alkyl substituents corresponds to a "p-menthane" structure as shown at page 706 of enclosed Exhibit A (Encyclopedia of Chemical Technology, Raymond E. Kirk Editor, vol 13, 1954, pp.705-727). Consequently, it is submitted that this rejection should be withdrawn.

Claims 13, 14, 24, 25, 35 and 36 have been rejected under 35 U.S.C. 112 and 101 as being improper method or process claims for failing to positively recite method or process steps. In response to these rejections, all of these claims have been amended (claims 24 and 35 having been canceled) such that these claims are now all appropriate "product" type claims satisfying all applicable requirements under 35 U.S.C. 112 and 101.

Claims 21 and 22 have been rejected under 35 U.S.C. 112, second paragraph, as allegedly being indefinite because of the use of the word "type". These claims have been amended so as to remove the term "type" such that this rejection should be withdrawn.

Claims 15, 16, 23 and 26-34 have been rejected under 35 U.S.C. 112, second paragraph, as allegedly being indefinite because the introductory phrase in these claims does not correspond to the introductory phrase recited in claim 1 from which these claims

depend. In response to this rejection, all of these claims have been appropriately amended such that the introductory phrases of all of these dependent claims are consistent with that of independent claim 1.

Claims 14 and 36 have been rejected as noted at pages 4-5 of the Office Action. These claims have been amended so as to appropriately recite an additional element thereby removing any possible antecedent bases issues.

**Removal of Issues Under 35 U.S.C. 102(b)**

Claims 1, 7, 8, 12, 17 and 20 have been rejected under 35 U.S.C. 102(b) as being anticipated by Sei '137 (USP 5,523,137). This rejection is traversed for the following reasons.

Sei '137 discloses an adhesive paper for tape automated bonding (TAB), wherein an example of a tape includes an insulating film (1), a semi-cured adhesive layer (2), and a protection film (3) as shown Figure 1. The adhesive layer may contain an epoxy resin as shown in column 5, line 33, which made be a "dicyclopentadiene dioxide" as noted at column 6, lines 20-25.

Sei '173 fails to disclose an adhesive sheet which includes an adhesive layer containing an epoxy resin which additionally contains glycidyl groups, wherein the epoxy resin may be a dicyclopentadiene skeleton-containing epoxy resin as recited in 1 of the embodiments of claim 1. Although, Sei '137 does disclose

some epoxy resins which contain glycidyl groups, Sei '137 fails to disclose or provide any suggestions for using a dicyclopentadiene dioxide which also contains glycidyl groups. Consequently, significant patentable distinctions exist between the present invention and Sei '137 such that the above-noted rejection should be withdrawn. In addition, it is submitted that Sei '137 fails to provide any adequate basis for a motivation to one skill in the art to include glycidyl groups in the dicyclopentadiene dioxide epoxy resin, such that there fails to be any adequate basis for alleging obviousness under 35 U.S.C. 103. Therefore, it is requested that the above-noted rejection be withdrawn and that no further prior art rejections be made based on Sei '137.

**Removal of Issues Under 35 U.S.C. 103(a)**

Claims 1, 4-6, 15, 16, 20 and 26-28 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Arai '908 (USP 5,827,908). This rejection is traversed for the following reasons.

Arai '908 discloses in Figure 1 a pre-molded package in the form of a hollow box (1) with a lead frame (2), a silicon chip (3) mounted in a hollow cavity of the package (1), bonding wires (4), and a transparent glass lid (5) which seals the opening of the package (1) within epoxy resin adhesive (6) as noted at column 18, lines 13-21.

Arai '908 fails to disclose or suggest an adhesive sheet for a semiconductor connecting flexible substrate which includes a laminate having an adhesive layer on a flexible substrate as in the present invention. The package shown in Figure 1 of Arai '908 fails to include any flexible substrate. It is further submitted that Arai '908 fails to provide any basis for a motivation to one skill in the art to employ a flexible substrate within adhesive layer, such that significant patentable distinctions exist between the present invention and Arai '908.

It is submitted for the reasons stated above that the presently pending claims defined patentable subject matter such that this application should be placed into condition for allowance.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact Andrew D. Meikle (Reg. No. 32,868) at the telephone number of the undersigned below.

**Attached hereto is a marked-up version of the changes made to the application by this Amendment.**

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. §§ 1.16 or 1.17; particularly, extension of time fees.

Respectfully submitted,

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Attachments: Marked Up Version of Claims  
Exhibit A

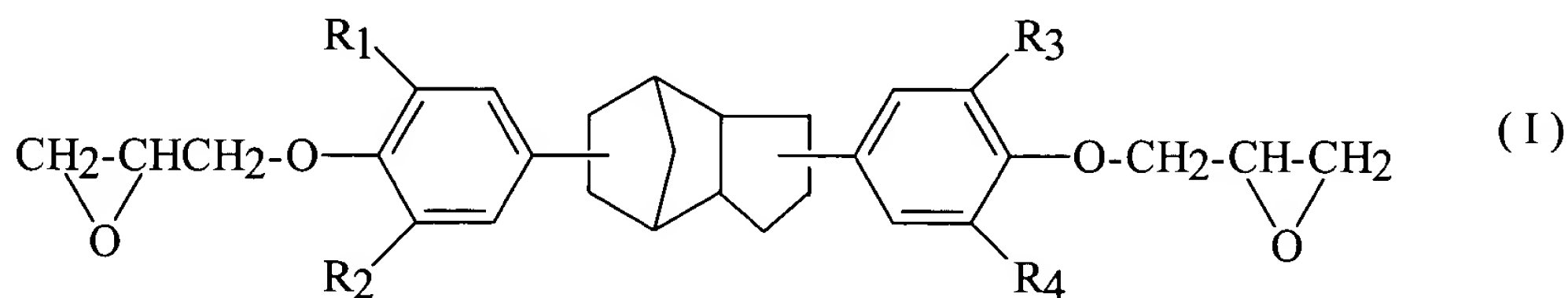
(Rev. 02/20/02)

Marked up Version of Claims

1. (Amended) An adhesive sheet for a semiconductor connecting flexible substrate ~~being constituted by~~ comprising a laminate having an adhesive layer on a flexible substrate, wherein said adhesive layer contains a thermoplastic resin (A) and an epoxy resin containing glycidyl groups (B), and said epoxy resin (B) contains at least one epoxy resin (B) selected from the following (I), (II), and (III) ~~and (IV)~~ as an essential component:

- (I) Dicyclopentadiene skeleton-containing epoxy resins,
- (II) Terpene skeleton-containing epoxy resins, and
- (III) Biphenyl skeleton-containing epoxy resins.

2. (Amended) An adhesive sheet for a semiconductor connecting substrate according to claim 1, wherein the dicyclopentadiene skeleton-containing epoxy resins (b1) are represented by the following general formula (I):



~~(in formula (1),~~ wherein  $R_1$  to  $R_4$  stand for a hydrogen atom, lower alkyl group with 1 to 4 carbon atoms or halogen atom.)

5. An adhesive sheet as claimed in claim 1 for a semiconductor connecting substrate which forms an adhesive layer (E) of a semiconductor integrated circuit board having at least, respectively, one wiring board layer (C) having an insulator layer and a conductor pattern, one layer without any conductor pattern formed (D) and one adhesive layer (E), wherein said adhesive sheet has a storage elastic modulus of 0.1 to 10000 MPa and a coefficient of linear expansion of  $0.1 \times 10^{-5} \sim 50 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$  in a temperature range of -50 to 150°C after having been cured by heating.

6. An adhesive sheet for a semiconductor connecting substrate according to claim 5, which has a breaking energy at 25°C of  $5 \times 10^5 \text{ Nm}^{-1}$  or more after having been cured by heating.

7. An adhesive sheet for a semiconductor connecting substrate having at least, respectively, one wiring board layer (C) being constituted by an insulator layer and a conductor pattern, one layer without any conductor pattern formed (D) and one adhesive layer (E), which forms an adhesive layer (E) of a semiconductor integrated circuit board, wherein said adhesive sheet contains at least, respectively, one thermoplastic resin (A) and one epoxy resin (B) as essential components, and said epoxy resin (B) contains at least one epoxy resin (B) selected from the following (I), (II), and (III) as an essential component:



- (I) Dicyclopentadiene skeleton-containing epoxy resins,
- (II) Terpene skeleton-containing epoxy resins, and
- (III) Biphenyl skeleton-containing epoxy resins.

8. An adhesive sheet for a semiconductor connecting substrate according to claim 7, wherein the thermoplastic resin (A) is a copolymer (a1) containing butadiene as an essential comonomer.

9. An adhesive sheet for a semiconductor connecting substrate according to claim 7, wherein the thermoplastic resin (A) contains a copolymer (a2) having butadiene as an essential comonomer and having carboxyl groups.

10. An adhesive sheet for a semiconductor connecting substrate according to claim 7, wherein the thermoplastic resin (A) is a polyamide resin (a3) containing a dicarboxylic acid with 36 carbon atoms as an essential component.

11. An adhesive sheet for a semiconductor connecting substrate according to claim 7, wherein the thermoplastic resin (A) is a polyamide resin (a3) containing a dicarboxylic acid with 36 carbon atoms as an essential component and is a polyamide resin (a4) having an amine value of more than 1 and less than 3.

12. An adhesive sheet for a semiconductor connecting substrate according to claim 7, which additionally contains a phenol resin (F).

13. (Amended) A semiconductor connecting substrate comprising ~~the use of~~ the adhesive sheet for a semiconductor connecting substrate stated in claim 7, wherein said semiconductor connecting substrate has at least, respectively, one wiring board layer ~~(C)~~ being constituted by an insulator layer and a conductor pattern (C), one layer without any conductor pattern formed (D) and one adhesive layer (E).

14. (Amended) A semiconductor device comprising ~~the use of~~ the semiconductor connecting substrate of ~~stated in~~ claim 13 and an integrated circuit.

15. (Amended) The adhesive sheet ~~An adhesive backed tape~~ for tape automated bonding TAB (TAB) being constituted by a laminate as claimed in claim 1, said laminate having an adhesive layer and a protective film layer on a flexible organic insulating film, wherein said adhesive layer has a softening temperature of 60 to 110°C after having been cured, and has an insulation resistance dropping time of 50 hours or more after having been allowed to stand in an environment of 130°C and 85% RH with DC 100 V applied.

16. (Amended) The adhesive sheet ~~An adhesive-backed tape~~ for TAB according to claim 15, wherein the adhesive layer has a breaking energy of  $5 \times 10^5 \text{ Nm}^{-1}$  or more at 25°C after having been cured by heating.

17. (Amended) An adhesive-backed tape for tape automated bonding ~~TAB~~ (TAB) being constituted by a laminate having an adhesive layer and a protective film layer on a flexible organic insulating film, wherein said adhesive layer contains a thermoplastic resin (A) and an epoxy resin (B) and said epoxy resin (B) contains at least one epoxy resin (B) selected from the following (I), (II), and (III) as an essential component:

- (I) Dicyclopentadiene skeleton-containing epoxy resins,
- (II) Terpene skeleton-containing epoxy resins, and
- (III) Biphenyl skeleton-containing epoxy resins.

18. An adhesive-backed tape for TAB according to claim 17, wherein the thermoplastic resin (A) is a polyamide resin (a) containing a dicarboxylic acid with 36 carbon atoms as an essential component.

19. An adhesive-backed tape for TAB according to claim 17, wherein the thermoplastic resin (A) is a polyamide resin (a)

containing a dicarboxylic acid with 36 carbon atoms as an essential component and is a polyamide resin (a') having an amine value of 1 or more and 3 or less.

20. An adhesive-backed tape for TAB according to claim 17, wherein the adhesive layer additionally contains a phenol resin (F).

21. (Amended) An adhesive-backed tape for TAB according to claim 20, wherein the phenol resin (F) contains more than 35 wt% and less than 60 wt% of a resol ~~type~~ phenol resin based on the weight of the adhesive layer.

22. (Amended) An adhesive-backed tape for TAB according to claim 21, wherein the resol ~~type~~ phenol resin contains a bifunctional phenol derivative (f1) with at least one alkyl group with 5 to 12 carbon atoms and a trifunctional or higher-functional phenol derivative (f2) as essential components, with the condition that  $f1/(f1 + f2) = 0.2 \sim 0.8$ .

23. (Amended) The adhesive sheet ~~An adhesive-backed tape~~ for TAB according to claim 15, wherein the organic insulating film is a polyimide film.

~~24. (Amended) A semiconductor connecting substrate comprising the use of the adhesive backed tape for TAB stated in claim 15.~~

25. (Amended) A semiconductor device comprising ~~the use of the adhesive-backed tape for TAB semiconductor connecting substrate~~ of ~~stated in claim 24~~ 15 and an integrated circuit.

26. (Amended) The adhesive sheet ~~An adhesive backed tape~~ for wire bonding connection being constituted by a laminate as claimed in claim 1, said laminate having an adhesive and a protective film layer on a flexible organic insulating film, wherein said adhesive layer has a softening temperature of 120 to 200°C after having been cured, a storage elastic modulus of 20 to 100 MPa at 150°C and an insulation resistance dropping time of 50 hours or more after having been allowed to stand in an environment of 130°C and 85% RH with DC 100 V applied.

27. (Amended) The adhesive sheet ~~An adhesive backed tape~~ for wire bonding connection according to claim 26, wherein the adhesive layer contains a thermoplastic resin (A) and an epoxy resin (B), and the film made of 1/1 mixture consisting of said thermoplastic resin (A) and said epoxy resin (B) is 8 to 40 in haze.

28. (Amended) The adhesive sheet ~~An adhesive backed tape~~ for wire bonding connection according to claim 26, wherein the adhesive layer contains a thermoplastic resin (A) and an epoxy resin (B) and said epoxy resin (B) contains at least one epoxy resin (B) selected from the following (I), (II) and (III) as an essential component:

- (I) Dicyclopentadiene skeleton-containing epoxy resins,
- (II) Terpene skeleton-containing epoxy resins, and
- (III) Biphenyl skeleton-containing epoxy resins.

29. (Amended) The adhesive sheet ~~An adhesive backed tape~~ for wire bonding connection according to claim 28, wherein the epoxy resin content is 10 wt% to 40 wt% based on the weight of the adhesive layer.

30. (Amended) The adhesive sheet ~~An adhesive backed tape~~ for wire bonding connection according to claim 28, wherein the thermoplastic resin (A) is a polyamide resin (a) containing a dicarboxylic acid with 36 carbon atoms as an essential component.

31. (Amended) The adhesive sheet ~~An adhesive backed tape~~ for wire bonding connection according to claim 28, wherein the thermoplastic resin (A) consists of a polyamide resin (a) containing a dicarboxylic acid with 36 carbon atoms as an essential

component an a polyamide resin (a') having an amide value of 1 or more and 3 or less.

32. (Amended) The adhesive sheet ~~An adhesive backed tape~~ for wire bonding connection according to claim 28, wherein the adhesive layer contains additionally a phenol resin (F).

33. (Amended) The adhesive sheet ~~An adhesive backed tape~~ for wire bonding connection according to claim 32, wherein the phenol resin (F) contains a resol type phenol resin of more than 35 wt% and less than 60 wt% based on the weight of the adhesive layer.

34. (Amended) The adhesive sheet ~~An adhesive backed tape~~ for wire bonding connection according to claim 26, wherein the organic insulating film is a polyimide film.

~~35. A semiconductor connecting substrate comprising the use of the adhesive backed tape for wire bonding connection stated in claim 26.~~

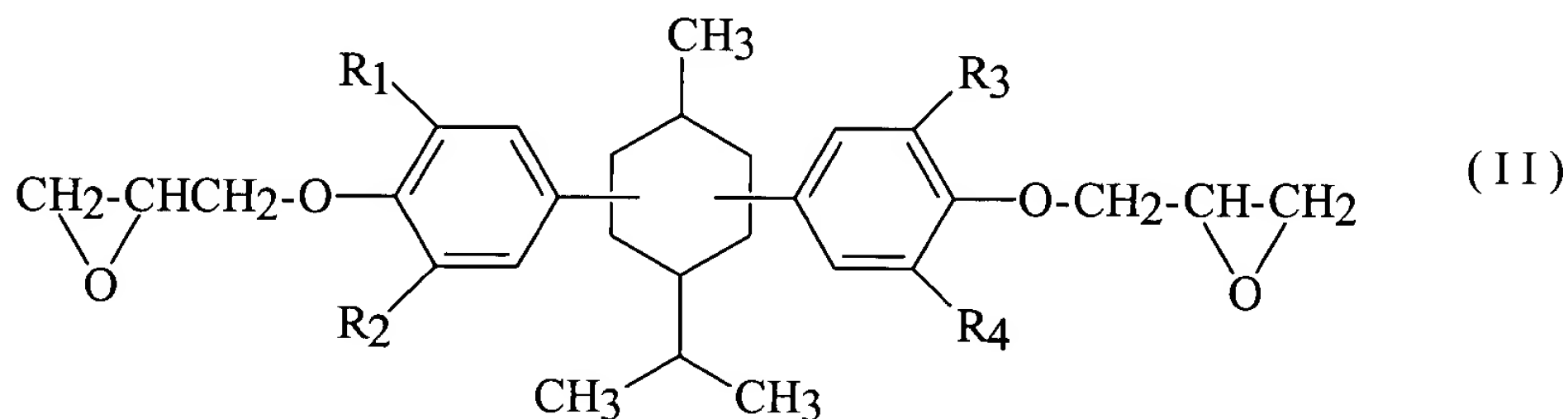
36. (Amended) A semiconductor device comprising ~~the use of the~~ adhesive-backed tape for wire bonding ~~semiconductor connecting substrate of stated in claim 35~~ 26 and an integrated circuit.

37. A semiconductor connecting substrate comprising the use of the adhesive sheet for a semiconductor connecting substrate according to claim 1.

38. A semiconductor device comprising ~~the use of the~~ the adhesive sheet semiconductor connecting substrate of according to claim 37 1 and an integrated circuit.

Please add the following new claims:

39. An adhesive sheet for a semiconductor connecting substrate according to claim 1, wherein the terpene skeleton-containing epoxy resins (b2) are represented by the following general formula (II):

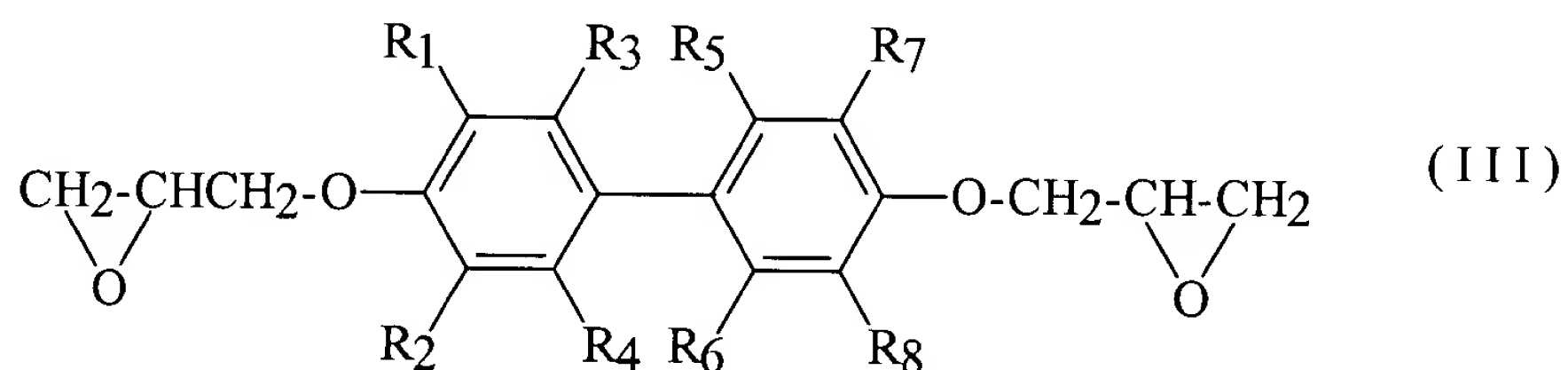


wherein  $R_1$  to  $R_4$  stand for a hydrogen atom, lower alkyl group with 1 to 4 carbon atoms, or halogen atom.

40. An adhesive sheet for a semiconductor connecting substrate according to claim 1, wherein the biphenyl skeleton-



containing epoxy resins (b3) are represented by the following general formula (III):



wherein R<sub>1</sub> to R<sub>8</sub> stand for, respectively independently, a hydrogen atom, lower alkyl group with 1 to 4 carbon atoms or halogen atom.

# ***ENCYCLOPEDIA*** **OF CHEMICAL** **TECHNOLOGY**

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**VOLUME 13**

***STILBITE***

*to*

***THERMOCHEMISTRY***

**Japanese Reprint Edition**

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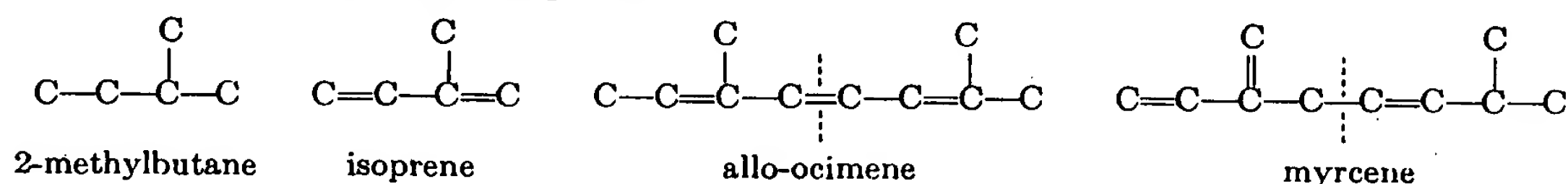
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## TERPENES AND TERPENOIDS

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Sesquiterpenoids.....	740		

The terpenes embrace a vast family of chemical compounds which are isolated chiefly from essential oils and resins of plants (see *Oils, essential*; *Resins, natural*). Strictly speaking, they are acyclic and cyclic hydrocarbons whose molecular formulas are some multiple of  $C_5H_8$ . Usually this definition is expanded to include naturally occurring and synthetic alcohols, aldehydes, ketones, and other derivatives having the same carbon skeleton as the parent terpene hydrocarbon and more properly called *terpenoids* (a term also used to include the terpenes proper). A characteristic feature of these hydrocarbons and their derivatives is the presence of the 2-methylbutane carbon structure as a recurring unit.



Most of the hydrocarbons (except the tricyclic  $C_{10}H_{16}$  members) are unsaturated, and they can be considered condensation products of isoprene,  $C_5H_8$  (see Vol. 7, p. 605); according to the *isoprene rule* noted by Wallach in 1887, these isoprene units are arranged head-to-tail, though there are some exceptions. The terpenes (and their derivatives) can therefore be classified according to the number of isoprene units—one, two, three, four or more—into hemiterpene (isoprene),  $C_5H_8$ ; monoterpenes,  $C_{10}H_{16}$ ; sesquiterpenes,  $C_{15}H_{24}$ ; diterpenes,  $C_{20}H_{32}$ ; and polyterpenes,  $(C_5H_8)_n$ , of which the most numerous are the  $C_{30}$  triterpenoids. Also included are some closely related compounds such as geraniolene,  $C_9H_{16}$ , and santene,  $C_9H_{14}$ , and their derivatives. The carotenoids ( $C_{40}$ ) (see "Vitamin A" under *Vitamins*), rubber and gutta percha (see Vol. 11, pp. 815, 825) are also isoprenoid compounds.

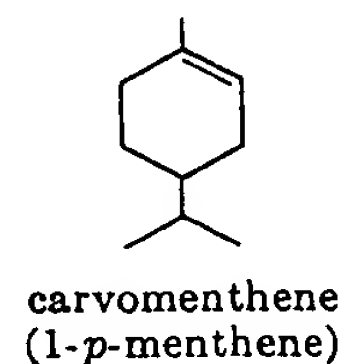
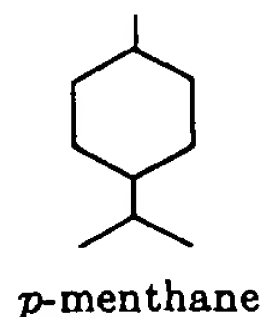
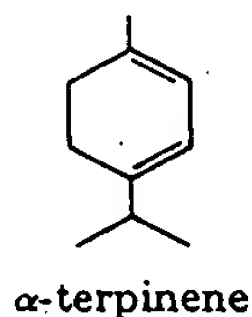
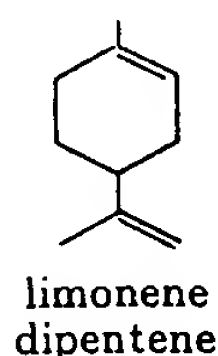
These classes of terpenes may be further subdivided into acyclic, monocyclic, bicyclic, etc. The degree of unsaturation depends upon the number of carbon atoms (number of isoprene units) and the number of rings, one double bond disappearing for each carbon-to-carbon bond formed. Thus in the monoterpenes the number of ethylenic linkages varies from none in the tricyclic hydrocarbons to three in the acyclic. *Isopropenyl-isopropylidene isomerism*, deriving only from the position of the double bond in the head of one of the isoprene units ( $CH_2=C(CH_3)-$  and  $(CH_3)_2C=$ ), is typical of many terpenoids (as limonene and  $\alpha$ -terpinene—see the formulas below), and the forms are distinguished only with difficulty particularly among the acyclic monoterpenes and their derivatives. Many other types of structural isomerism exist among the terpenes (see, for example, the formulas for bicyclic and tricyclic monoterpenes below), as well as both types of stereoisomerism, optical and geometrical.

**Nomenclature and Formulas.** The common names of most terpenoids are derived from the botanical origins of the compounds, and the designations  $\alpha$ -,  $\beta$ -,  $\gamma$ -, etc., are used merely to differentiate isomers without positional significance. The structural formulas for ring compounds are usually written without showing carbon or hydrogen atoms, a bond attached to a ring denoting a methyl group and a double bond a methylene group (see below). Even acyclic compounds are frequently written similarly, in partial ring form, particularly to bring out relationships to cyclic compounds. Formulas for polycyclic terpenoids once were always oriented in the opposite way from sterols and steroids (*q.v.*), that is, from the upper left to the lower right, but di- and especially triterpenoid

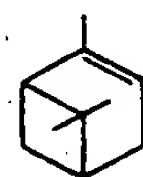
formulas are more and more being oriented and numbered like the steroids as stereochemical relationships are elucidated.

The **monoterpenoids** ( $C_{10}$ ) are subdivided into acyclic, monocyclic, bicyclic, and tricyclic monoterpenoids. The *acyclic* terpenes, of which allo-ocimene and myrcene are examples, are aliphatic hydrocarbons containing three olefinic double bonds.

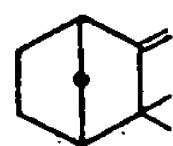
The *monocyclic* terpenes, for example, limonene (or its optically inactive isomer dipentene) and  $\alpha$ -terpinene, contain one six-membered ring. They contain two double bonds, but other compounds such as *p*-menthane and carvomenthene (1-*p*-menthene), having the same carbon skeleton, are included in common usage.



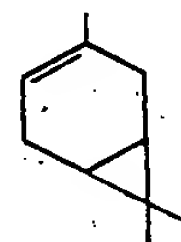
The *bicyclic* terpenes, of which  $\alpha$ -pinene, camphene, and 3-carene are examples, contain two fused rings and one double bond:



$\alpha$ -pinene

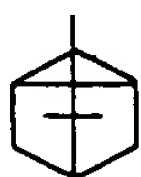


camphene

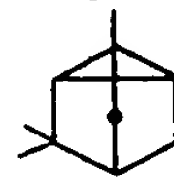


3-carene

The *tricyclic* terpenes differ from the bicyclic terpenes in having an additional carbon-carbon bond or bridge instead of an olefinic double bond. Tricyclene and cyclofenchene are examples of this class:

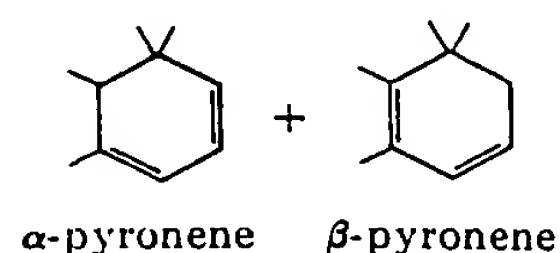
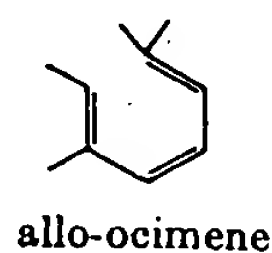


tricyclene

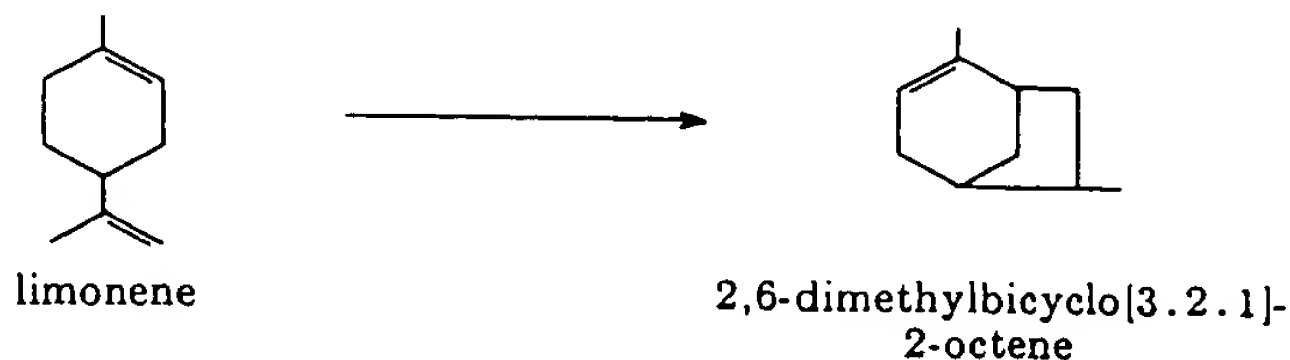


cyclofenchene

These classes of monoterpenes are closely related and one class is frequently prepared from the other. Under acid isomerization conditions, for example,  $\alpha$ -pinene, a bicyclic terpene, forms monocyclic and tricyclic terpenes in addition to isomeric bicyclic terpenes, as in the synthesis of camphene (p. 728). Thermal cracking of  $\alpha$ -pinene forms acyclic and monocyclic terpenes, as in the chief synthesis of allo-ocimene. The conversion of acyclic to monocyclic hydrocarbons and of monocyclic to bicyclic hydrocarbons is less common than the reverse processes (although acyclic alcohols and aldehydes are readily cyclized to unsaturated derivatives of *p*-menthane or of 1,1,3-trimethylcyclohexane; see, for example under "Citral" p. 717). Allo-ocimene is, however, converted to the cyclic pyronenes by thermal cyclization:



Myrcene is similarly converted to camphorene, a monocyclic diterpene (see p. 758). In addition, monocyclics have been converted to bicyclics by acid polymerization:



However, the conversions to pyronenes and the bicyclooctene are not reversals of the ring-opening processes since the carbon skeletons of the products differ from those of the naturally occurring monocyclic and bicyclic terpenes.

The **sesquiterpenoids** ( $C_{15}$ ) of known constitution exhibit an even greater variety of structure than the monoterpenes, and the structures of many are still unknown. Among those well characterized are *acyclic* alcohols and *monocyclic* hydrocarbons, alcohols, and one quinone, both of these subclasses containing three olefinic linkages; *bicyclic* compounds derived from naphthalene, azulene (cyclopentacycloheptene), and other fused ring systems and containing one or two olefinic linkages; and *tricyclic* hydrocarbons and alcohols containing one olefinic linkage. One ketone, eremophilone (see p. 750), derived from naphthalene and containing two olefinic linkages, is a notable exception to the isoprene rule because of an angular methyl group on a carbon adjacent to another bearing a methyl group. Because of a certain amount of interconversion among the above types of sesquiterpenoids, a division based on the dehydrogenation products (derivatives of naphthalene, azulene, etc.) is considered preferable to one based on the number of rings.

Still less is known about the **diterpenoids** ( $C_{20}$ ) as a whole than about the sesquiterpenoids. However, well-characterized compounds include the *acyclic* alcohol phytol, containing one double bond; the *monocyclic* hydrocarbon camphorene, with four double bonds; and a number of *bicyclic* and *tricyclic* acids, alcohols, and phenols, containing for the most part two double bonds, the best known of these compounds being the tricyclic resin acids of the abietic and pimaric types. As with the sesquiterpenoids, the most satisfactory division is based on dehydrogenation reactions, since the bicyclic compounds after cyclization give the same dehydrogenation products as the tricyclic compounds. These products are retene (7-isopropyl-1-methylphenanthrene), formed by the abietic-type acids; pimanthrene (1,7-dimethylpimanthrene), from the pimaric-type acids; and 1,7,8-trimethylphenanthrene, first obtained from a derivative of agathic acid, a bicyclic resin acid. See also *Rosin*.

Some **triterpenoid** ( $C_{30}$ ) saponins (*q.v.*) have not been well characterized, but the triterpenoids themselves have been and form a very large group. They include two compounds obtained from animal sources: the *acyclic* hydrocarbon squalene (from fish oils) containing six double bonds, and the *tricyclic* alcohol ambrein (from ambergris), containing two double bonds. The *tetracyclic* compounds, principally the alcohols lanosterol and agnosterol (from wool grease) have recently been found to be nonisoprenoid and closely related to sterols (*q.v.*) such as cholesterol. The largest division of the triterpenoids therefore consists of the *pentacyclic* compounds, containing one double bond; this bond is in the middle ring in the  $\beta$ - and  $\alpha$ -amyrin groups and is comparatively inactive, whereas in the lupeol-betulin and taraxasterol groups it is in an isopropenyl group or in the terminal ring (E) and is active. Although these



pentacyclic compounds are isoprenoid, they have also been related stereochemically to the steroids.

**Uses.** Many of the terpenes, principally the monoterpenes, are important articles of commerce and are used directly or are the raw materials for the preparation of perfumes (*q.v.*), flavors (*q.v.*), protective coatings, pharmaceuticals, insecticides, bactericides, flotation agents, condensation catalysts, extreme-pressure lubricant additives, adhesives, solvents, and plasticizers. The importance of terpenes may be judged from the figure of 28,233,500 gal. of turpentine (chiefly bicyclic monoterpenes) produced in the United States during the naval stores year April 1952–March 1953 (see *Turpentine*). Although in the past the major use of terpenes has been as solvents, they are becoming increasingly important for chemical synthesis.

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W. S. ROPP

### MONOTERPENOIDS—ACYCLIC

This section includes the naturally occurring hydrocarbons, alcohols, aldehydes, ketones, and closely related compounds, including some monocyclic ketones derived from citral, an acyclic aldehyde. A number of the alcohols and aldehydes constitute

TABLE I. Production and Sales of Industrially Important Acyclic Monoterpenoids (1953).

Commodity	Production, 1000 lb.	Sales		Unit value per lb.
		Quantity, 1000 lb.	Value, \$1000	
Citral.....	53	48	139	2.91
Citronellal.....	—	1	1	1.68
Citronellol.....	183	165	250	1.51
Citronellyl acetate.....	—	3	7	2.25
Citronellyl propionate.....	3	3	16	5.23
Geraniol.....	551	521	436	0.84
Geranyl acetate.....	30	27	35	1.32
Geranyl formate.....	2	2	8	4.02
Hydroxycitronellal.....	148	118	472	4.00
$\alpha$ -Ionone.....	10	9	47	5.36
$\beta$ -Ionone.....	111	69	290	4.18
Ionone ( $\alpha$ - and $\beta$ -).....	38	34	101	2.95
Linalool.....	251	48	238	4.93
Linalyl acetate.....	120	89	449	5.02
Methyl- $\alpha$ -ionone.....	77	66	321	4.88
Methylionone ( $\alpha$ - and $\beta$ -).....	52	59	264	4.47
Nerol.....	2	2	19	9.32
Rhodinol.....	8	6	59	25.73

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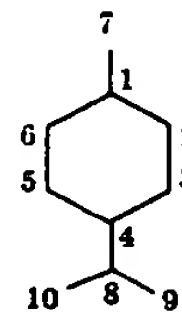
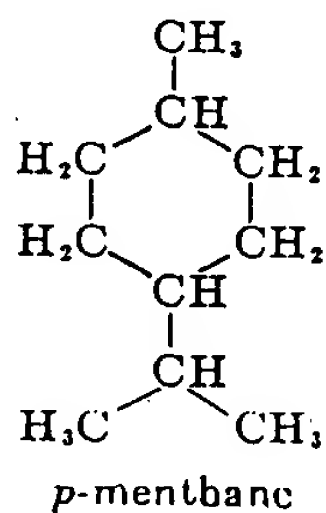
J. E. HAWKINS AND E. G. RIETZ

## MONOTERPENOIDS—CYCLIC

## Monocyclic Hydrocarbons

The monocyclic terpenes constitute a large group of isomeric compounds which are of interest as such and as the parent hydrocarbons for a variety of derivatives containing functional groups.

The monocyclic terpene hydrocarbons are chiefly compounds having the carbon skeleton of *p*-menthane (1-methyl-4-isopropylcyclohexane):



*p*-Menthane and several of the other terpenes and terpene derivatives exist in *cis* and *trans* forms which differ enough in physical properties to allow isolation by physical means. Those terpenes containing one or more asymmetric carbons also exhibit optical isomerism.

The monocyclic terpenes for which no historical names have been established are named systematically as menthenes or menthadienes using the fixed numbering system shown.

The skeleton structural formulas of the principal monocyclic terpenes are given in Figure 1.



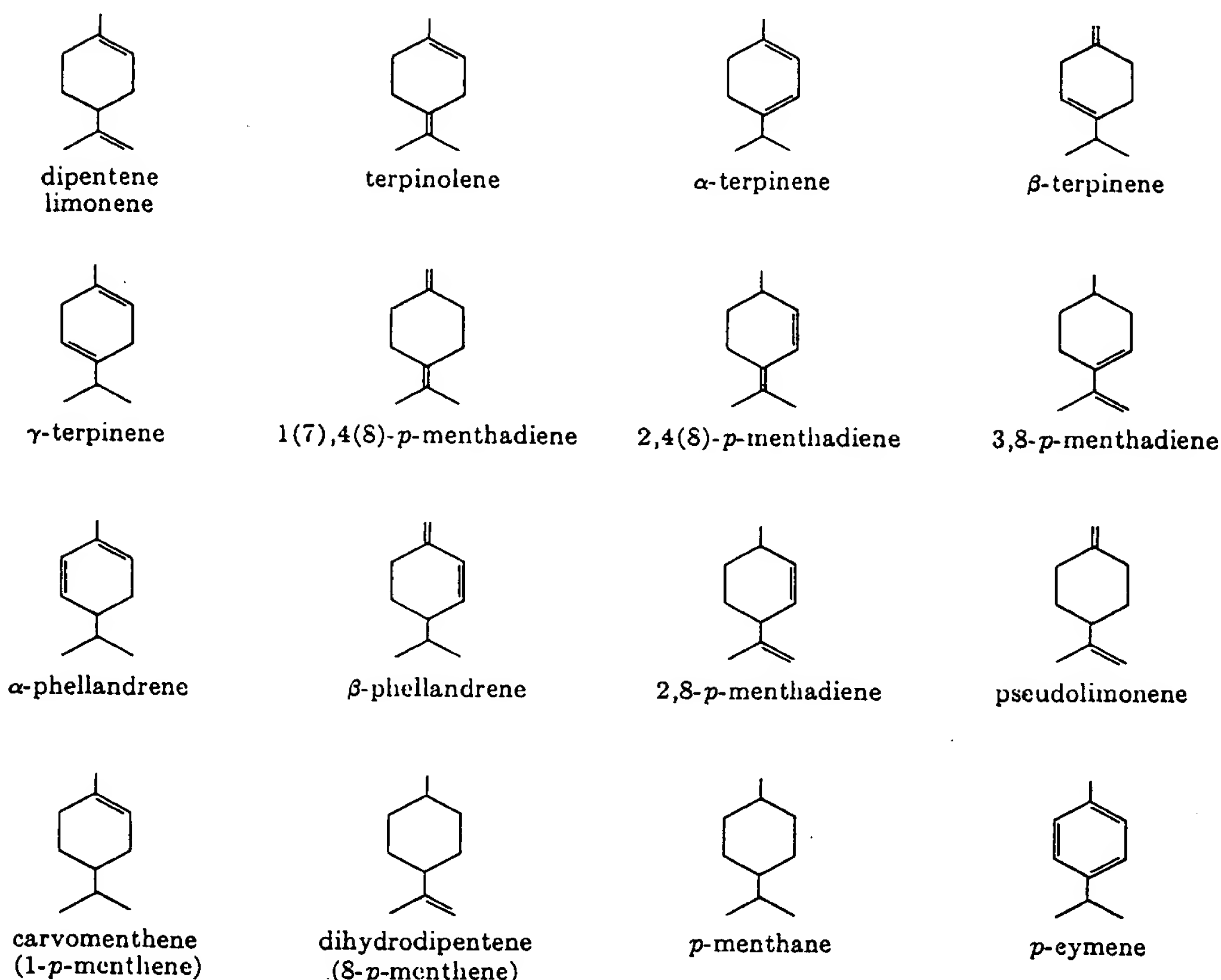


Figure 1.

## PHYSICAL AND CHEMICAL PROPERTIES

The difficulty of obtaining terpenes free from isomeric compounds has hindered attempts to obtain reliable physical properties. The use of more efficient distillation equipment coupled with improved methods of instrumental analysis has, however, allowed a considerable improvement. Some physical properties of the principal monocyclic terpenes are reported in Table I (6,21,22).

The chemical properties of monocyclic terpenes are not unique but rather are those that might be expected from their structures. In the case of the menthenes and menthadienes, the majority of the reactions are those that involve the double bonds or the allylic hydrogens (hydrogens on carbons alpha to double bonds). Catalytic hydrogenation yields *cis*- and *trans-p*-menthane. Addition of halogens or hydrogen halides yields the corresponding alicyclic halides; free-radical chlorination yields polyhalides. Heating with sulfur forms complex sulfurized compounds. This reaction is the basis for sulfurized terpene extreme-pressure lubricant additives. Treatment with many acids, acid clays, and metallic halides yields isomerized olefins and dimeric terpenes. Reaction with oxygen yields hydroperoxides which frequently react further to yield alcohols, ketones, and acids. *p*-Menthane hydroperoxide is produced commercially by this reaction. Reaction with maleic anhydride (see Vol. 1, p. 527; Vol. 8, p. 682) yields Diels-Alder adducts of the conjugated diolefins. The nonconjugated diolefins react probably by isomerization to conjugated diolefins and by re-

TABLE I. Physical Properties of Monocyclic Terpene Hydrocarbons.

Compound	B.p., °C.		$n_D^{20}$	$d_4^{20}$
	760 mm.	100 mm.		
Dipentene	176.5	110 <sup>a</sup>	1.4730 <sup>a</sup>	0.8447 <sup>a</sup>
Terpinolene	186 <sup>a</sup>	120 <sup>a</sup>	1.4895 <sup>a</sup>	0.8620 <sup>a</sup>
$\alpha$ -Terpinene	175	108	1.4790	0.8353 <sup>19</sup>
$\beta$ -Terpinene	—	—	1.4750 <sup>25</sup>	0.8356 <sup>25</sup>
$\gamma$ -Terpinene	—	116 <sup>a</sup>	1.4754	0.851
2,4(8)- <i>p</i> -Menthadiene	—	120 <sup>a</sup>	1.5057 <sup>a</sup>	0.8592 <sup>a</sup>
3,8- <i>p</i> -Menthadiene	—	117.5 <sup>a</sup>	1.4874 <sup>25a</sup>	0.8498 <sup>25</sup>
$\alpha$ -Phellandrene	—	—	1.4702 <sup>25</sup>	0.8284 <sup>25</sup>
$\beta$ -Phellandrene	—	—	1.4851 <sup>25</sup>	0.8375 <sup>25</sup>
Carvomenthene	176 <sup>a</sup>	110 <sup>a</sup>	1.4572 <sup>a</sup>	0.8490 <sup>30</sup>
<i>p</i> -Cymene	177	110 <sup>a</sup>	1.4905 <sup>a</sup>	0.857
<i>cis-p</i> -Menthane	—	105	1.4431	0.8084 <sup>a</sup>
<i>trans-p</i> -Menthane	170 <sup>a</sup>	103	1.4367 <sup>a</sup>	0.7938 <sup>a</sup>
2- <i>p</i> -Menthene	169	—	1.4499	—
3- <i>p</i> -Menthene	169	102 <sup>a</sup>	1.4519	—
4(8)- <i>p</i> -Menthene	176	110 <sup>a</sup>	1.4689	—
8- <i>p</i> -Menthene	169	—	1.4454	0.819

<sup>a</sup> Values from the Laboratories of Hercules Powder Co.

action with the allylic hydrogens (see Vol. 8, p. 688). Reaction with aromatic hydrocarbons and phenols in the presence of Friedel-Crafts catalysts yields alkylated compounds. The menthadienes can be dehydrogenated to *p*-cymene or disproportionated to *p*-cymene and *p*-menthane. Hydration with sulfuric acid catalyst yields alcohols and glycols. Addition of nitrosyl chloride yields the nitrosochlorides, which are used to characterize terpenes (see Vol. 9, p. 468). Ozonolysis cleaves the double bond to yield aldehydes, ketones, and acids.

Specific compounds have additional reactions. For example, dipentene can be cracked to yield a mixture including isoprene. *p*-Cymene can be further dehydrogenated to yield  $\alpha$ ,*p*-dimethylstyrene.

#### OCCURRENCE

The most important monocyclic terpene industrially is limonene and its optically inactive (*dl*- or racemic) form dipentene. *dextro*-Limonene (carvene, hesperidene) and *levo*-limonene occur in many essential oils such as dill, caraway, and star anise. The principal commercial sources are the oils of orange, grapefruit, and lemon from which it may be obtained readily in over 90% purity. Dipentene occurs in a variety of essential oils such as bergamot, citronella, and nutmeg. The chief domestic sources are wood and sulfate turpentine (*q.v.*) from the southern pine (*Pinus palustris* and *P. caribaea*). Dipentene is formed together with other monocyclic terpenes as a major by-product in many acid-catalyzed reactions of  $\alpha$ -pinene such as its isomerization to camphene by an acidic clay. Dipentene is also formed together with acyclic terpenes by thermal cracking of  $\alpha$ -pinene.

Several of the sources of dipentene are also sources of other monocyclic terpenes. Thus, the monocyclic terpene fraction extracted from pinewood stumps contains terpinolene, *p*-cymene, *p*-menthanes, 2,4(8)-*p*-menthadiene, and  $\alpha$ -terpinene, as well as dipentene and small amounts of other isomers. The monocyclic terpenes formed by

acid-catalyzed reactions of  $\alpha$ -pinene contain terpinolene, 2,4(8)-*p*-menthadiene,  $\alpha$ -terpinene, and  $\gamma$ -terpinene in addition to dipentene.

#### MANUFACTURE

*From Orange Oil.* With the increases in the amount of citrus fruits that are processed to produce liquid or frozen canned juices, orange oil (chiefly *dextro*-limonene) from the peel has become available in moderate quantities. The volume of orange oil produced in 1951 has been estimated at 2,600,000 lb. Cold-pressed citrus oil is obtained from whole oranges by breaking the oil sacs or by crushing the peel. Distilled orange oils are obtained by vacuum-stripping citrus juices or by distilling citrus press liquor which is removed during the production of dry citrus pulp for cattle feed. Details of the procedure are given in a bulletin of the Florida Agriculture Experiment Station (13).

*From Pine Stumps.* The extraction of rosin and terpenes from wood stumps is described under *Rosin and rosin derivatives* (see Vol. 11, pp. 780-81). The total extract is distilled to yield the extracting solvent, bicyclic terpenes, monocyclic terpenes, pine oil, and the residual crude rosin. The monocyclic terpene fraction may be fractionally distilled under a variety of conditions to yield **dipentene**, **terpinolene**, and other fractions.

*From Other Sources.* Dipentene can be produced from  $\alpha$ -pinene by thermal cracking. The by-products include allo-ocimene and pyronenes. (See pp. 713, 729.) Dipentene is also formed as a by-product in the majority of acid-catalyzed reactions of  $\alpha$ -pinene such as isomerization to camphene and hydration to synthetic pine oil. The acid conditions, however, are usually drastic enough to produce other by-product terpenes and particularly  $\alpha$ - and  $\gamma$ -terpinene.

***p*-Menthane** and ***p*-cymene** have been produced by disproportionation of mixed monocyclic terpenes with catalysts such as platinum or palladium. ***p*-Menthane** has been produced by hydrogenation of monocyclic terpenes using a nickel catalyst.

#### ECONOMIC ASPECTS

During World War II steam-distilled dipentene had a ceiling price of \$0.56 per gallon for carloads of drums delivered in the East (U.S.). Prices since the war have fluctuated widely as illustrated by the quotations below, also for carloads of drums (18):

Date	Price, \$/gal.
July 1947	0.80 warehouse, N.Y.C.
July 1951	0.35 works, South
July 1954	0.64 works, South

The production of dipentene and other monocyclic terpenes is given in Table II (15).

#### ANALYSIS

Terpene hydrocarbon mixtures are characterized by A.S.T.M. boiling range, refractive index, specific gravity, bromine number, kauri-butanol value (see Vol. 11, p. 676), and other common physical and chemical constants. Before the advent of instruments such as the infrared and ultraviolet spectrophotometers, the analyses of terpene mixtures for individual components required the preparation of characteristic

TABLE II. U.S. Production of Monocyclic Terpenes.

Naval stores years <sup>a</sup>	Dipentene, thousand gallons	Other monocyclic hydrocarbons, thousand gallons
1942-43	1,227	1,797
1943-44	920	1,745
1944-45	932	1,686
1945-46	970	1,686
1946-47	1,366	2,006
1947-48	1,349	1,882
1948-49	1,309	1,974
1949-50	1,486	2,202
1950-51	2,232	2,527
1951-52	1,962	2,949
1952-53	1,795	2,361

<sup>a</sup> April to March.

derivatives with maleic anhydride, nitrosyl chloride, bromine, hydrogen chloride, or other reagents. The preparation of these derivatives in some cases serves also as a method for separation, although distillation is frequently needed before identification.

Although instrumental analysis has simplified the problem, it is still frequently necessary to use all the tools at hand to obtain a satisfactory material balance. One of the largest problems is the preparation of suitable standards. To obtain a quantitative analysis by ultraviolet, infrared, or mass spectroscopy it is necessary to have samples of the components in high purity. These reference standards should be stored in glass in the absence of light, air, and heat. Analysis of simple mixtures can sometimes be obtained without resorting to separation techniques. For example, where only one component contains conjugated unsaturation, its amount may be determined by ultraviolet analysis. Infrared absorption analysis is of more general usefulness but is generally less accurate because of the high probability of interfering absorption bands. The mass spectrometer is of general usefulness but is of particular advantage where the desired component has a different mass from the other components of the mixture. Thus, *p*-menthane as a contaminant in pinane can be quantitatively determined if the *cis-trans* isomer ratio is known. In most cases a more accurate figure is obtained by fractional distillation prior to analysis. The efficiency of fractionation required will,

TABLE III. Typical Physical Properties of Commercial Dipentenenes.

Property	Commercial dipentene		
	A	B	C
$d_{4.0}^{15.6}$	0.8518	0.8510	0.851
$n_D^{20}$	1.4739	1.4735	1.475
Unpolymerized residue, %	1.4	3.0	1.0
Flash point, °F.	126.0 <sup>a</sup>	130	117 <sup>b</sup>
Kauri-butanol value	62	63	70
Distillation range, °C.			
5%	176.0	174.0	175
50%	177.3	177.0	176
95%	181.0	183.0	178

<sup>a</sup> Cleveland open cup.<sup>b</sup> Tag open cup.



of course, vary with the mixtures, but usually the maximum efficiency available up to at least 100 plates is not excessive. This increases manifold the cost of analysis and, where repeated analyses are to be carried out on similar materials, the method is not practical. Even in these cases, fractional distillation should be used once to establish what components are present and the accuracy of the analysis on the original mixture.

*Typical Analyses.* The physical properties of three commercial dipentenes are given in Table III. The properties of additional terpene solvents may be found in manufacturers' bulletins (5,7,11,17,23).

The chemical composition of a typical commercial dipentene is:

Component	Amount, %
$\alpha$ - and $\beta$ -Pinene	5
<i>p</i> -Menthane	14
$\alpha$ -Terpinene	5
<i>p</i> -Cymene	17
Dipentene	51
Terpinolene	5
2,4(8)- <i>p</i> -Menthadiene	2
Fenchone	1

The physical properties of three commercial monocyclic terpene mixtures are given in Table IV.

TABLE IV. Typical Physical Properties of Solvent-Grade Monocyclic Terpenes.

Property	Commercial terpene solvents		
	D	E	F
$d_{15.6}^{15.6}$	0.8603	0.8565	0.8754
$n_D^{20}$	1.4755	1.4730	1.4802
Unpolymerized residue, %	0.5	1.8	—
Flash point, °F.	130 <sup>a</sup>	—	136
Kauri-butanol value	70	—	128
Distillation range, °C.			
5%	175.8	169.8	180.6
50%	178.4	173.4	185.4
95%	187	189.0	195.0

<sup>a</sup> Cleveland open cup.

### USES

The largest uses of monocyclic terpene mixtures are as solvents. One large use is in rubber reclaiming where they serve to swell the scrap rubber. Their ability to dissolve rubber renders them useful in making rubber-based solvent cements (adhesives). Mixed terpenes are used as solvents for paints, varnishes, and other protective coatings. They are higher boiling and have lower aniline points than turpentine. In oleoresinous finishes they function as antiskinning agents.

In general, dipentene can be used where terpene mixtures are satisfactory. It is usually a more desirable raw material than the less pure terpene mixtures for making sulfurized extreme-pressure lubricating-oil additives and synthetic resins. It is a logical starting material for chemical synthesis of isoprene, *p*-cymene, *p*-menthane, and carvomenthene. Both dipentene and carvomenthene can be used for alkylation of phenols by ionic catalysts. The molecular weights of the products from diolefins

are higher than expected because of dimerization through one of the terpene double bonds. Terpene-phenol resins so prepared (or more often from bicyclic terpenes, chiefly pinene) are used in printing inks, adhesives, and protective coatings. The products from dipentene or mixed monocyclics with phenol are antioxidants for rubber.

*p*-Menthane is a raw material for conversion to *p*-menthane hydroperoxide, the chief initiator used in making the so-called "cold" rubber (10), prepared at 5°C. See Vol. 11, pp. 832-33.

*p*-Cymene is used as a raw material for preparing *p*-cymene hydroperoxide, which in turn may be converted to *p*-cresol. It can, like *p*-xylene, be oxidized to terephthalic acid.

Mixtures of monocyclic terpenes are treated with maleic anhydride to prepare dibasic acids which are used in the preparation of alkyd resins for protective coatings (see Vol. 1, p. 527).

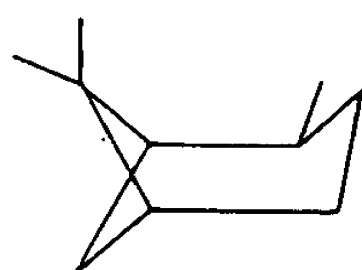
Orange oil (principally *dextro*-limonene) is used as a flavoring material in beverages, pharmaceuticals, extracts, and food.

*Terebene*, a mixture of terpenes containing chiefly dipentene and terpinenes, is used as an expectorant (see Vol. 5, p. 684).

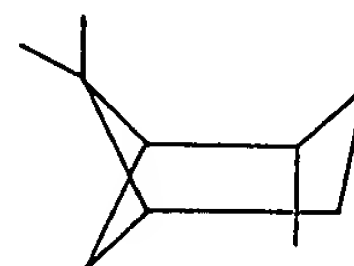
### Bicyclic and Tricyclic Hydrocarbons

The bicyclic terpenes are the most important class of terpenes from a commercial viewpoint. Tricyclic terpenes are of minor importance as such but are present as components of commercial terpene mixtures.

The bicyclic and tricyclic terpenes contain two and three rings respectively. Like the monocyclic terpenes many bicyclic terpenes, for example, pinane, exist in *cis* and *trans* forms (as well as optically active forms):



*cis*-pinane



*trans*-pinane

Their close structural relationship to the monocyclic and acyclic terpenes is illustrated by the fact that thermal rearrangement of  $\alpha$ -pinene, a bicyclic terpene, forms dipentene, a monocyclic terpene, and allo-ocimene, an acyclic terpene. The bicyclic terpenes are designated by trivial names; however, a more systematic system has been proposed (8). The skeleton formulas of the principal bicyclic and tricyclic terpenes are given in Figure 2.

### PHYSICAL AND CHEMICAL PROPERTIES

The determination of the physical properties of the bicyclic and tricyclic terpenes is subject to the difficulties previously described for the monocyclic terpenes. See Table V (21).

The reactivity of bicyclic terpenes is qualitatively similar to that of the monocyclic terpenes. They are unique, however, in their tendency in the presence of a

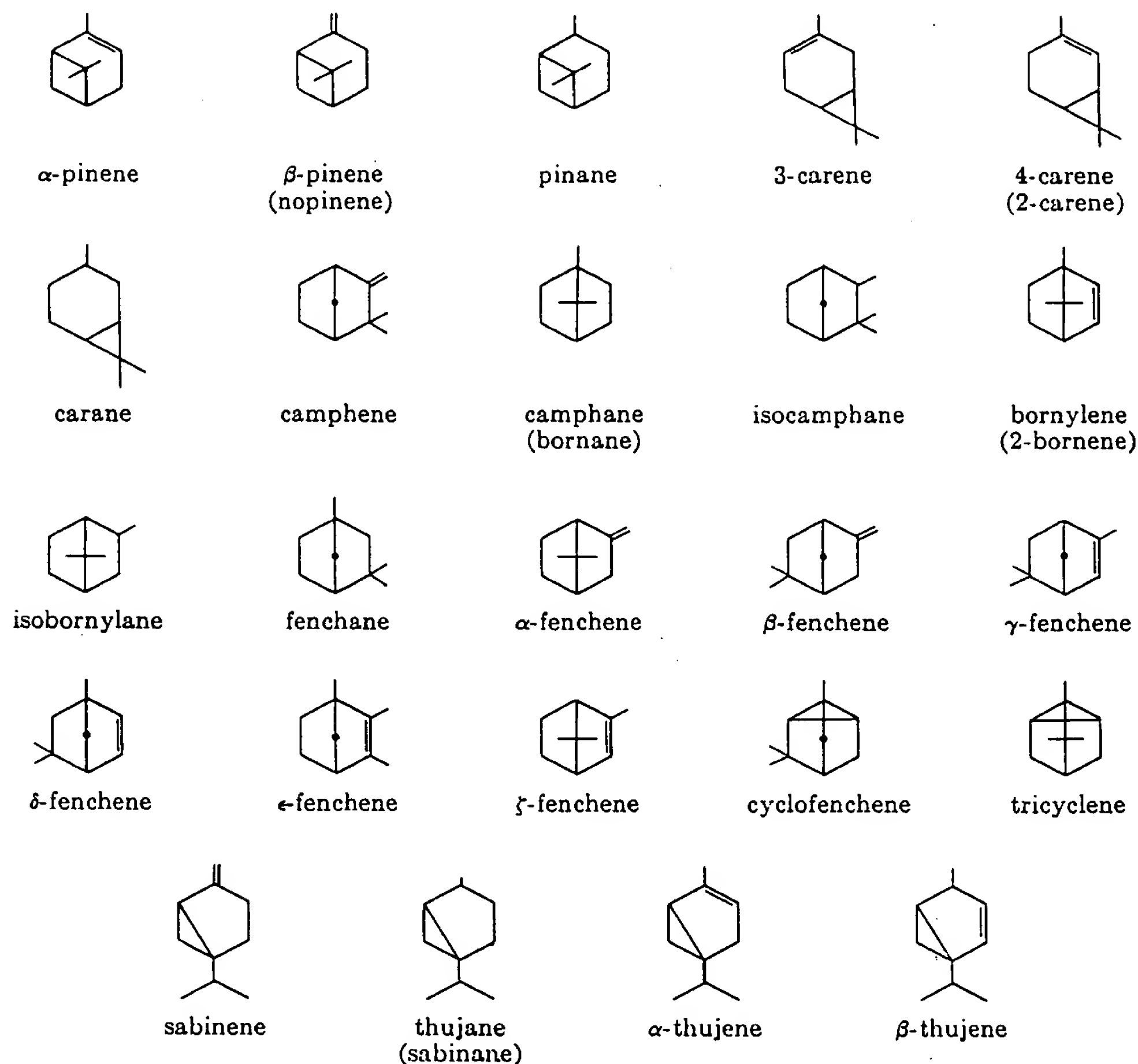


Figure 2.

TABLE V. Physical Properties of Bicyclic Terpenes.

Compound	B.p., °C.		M.p., °C.	$n_D^{20}$	$d_4^{20}$
	760 mm.	100 mm.			
$\alpha$ -Pinene	156 <sup>a</sup>	89	—	1.4658 <sup>a</sup>	0.8595 <sup>a</sup>
$\beta$ -Pinene	165 <sup>a</sup>	98 <sup>a</sup>	—	1.4790 <sup>a</sup>	0.8722 <sup>a</sup>
<i>cis</i> -Pinane	168 <sup>a</sup>	101 <sup>a</sup>	—	1.4628 <sup>a</sup>	0.8576 <sup>a</sup>
3-Carene	170	104 <sup>a</sup>	—	1.4730 <sup>a</sup>	0.8617
Camphene	158 <sup>a</sup>	91 <sup>a</sup>	49 <sup>a</sup>	1.4695 <sup>25</sup>	0.8675 <sup>25</sup>
Camphane	158 <sup>a</sup>	—	154	—	—
Isocamphane	166 <sup>a</sup>	100 <sup>a</sup>	65 <sup>a</sup>	—	—
Bornylene	146	—	113 <sup>a</sup>	—	—
$\alpha$ -Fenchene	157 <sup>a</sup>	91.5 <sup>a</sup>	—	1.4692 <sup>30</sup>	—
$\beta$ -Fenchene	151	—	—	1.4645 <sup>18-6a</sup>	0.8591
$\gamma$ -Fenchene	146	—	—	1.4607	0.8547
$\delta$ -Fenchene	139	—	—	1.4494	0.8381
$\epsilon$ -Fenchene	152	—	—	—	—
$\zeta$ -Fenchene	146.5	—	—	1.4685	0.8626
Cyclofenchene	143 <sup>a</sup>	78 <sup>a</sup>	—	1.4459 <sup>30</sup>	0.8595
Tricyclene	152 <sup>a</sup>	106.5 <sup>200a</sup>	65 <sup>a</sup>	1.4625	—
Sabinene	—	—	—	1.4636 <sup>25</sup>	0.8358 <sup>25</sup>
$\alpha$ -Thujene	—	—	—	1.4493 <sup>25</sup>	0.8261 <sup>25</sup>

<sup>a</sup> Values from the Laboratories of Hercules Powder Co.